Jarosite stability on Mars

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Abstract

Jarosite, a potassium (sodium) iron sulphate hydrated mineral, has recently been identified on the martian surface by the Opportunity rover. Using recent thermochemical data [Drouet and Navrotsky, 2003, Geochim. Cosmochim. Acta 67, 2063–2076; Forray et al., 2005, Geochim. Cosmochim. Acta, in press], we calculate the equilibrium decomposition curve of jarosite and show that it is thermodynamically stable under most present martian pressures and temperatures. Its stability makes jarosite potentially useful to retain textural, chemical, and isotopic evidence of past history, including possible biological activity, on Mars.

Keywords: Mars climate; Mineralogy; Jarosite; Mineral stability

1. Introduction

Jarosite, a hydrated sulphate of iron and potassium ($KFe_3(SO_4)_2(OH)_6$) is a widespread mineral on Earth Alpers et al., 1989, Stoffregen et al., 2000 and Dill, 2001, mainly formed in acid, sulphate rich environments associated with acid mine drainage and also commonly found in hydrometallurgical processes (Dutrizac and Jambor, 2000). Due its low solubility in water (Baron and Palmer, 1996), jarosite is a potential scavenger of heavy metals Dutrizac et al., 1996, Gieré et al., 2003 and Dutrizac, 2004, and plays an important role in the fate and transport of heavy metals in the environment.

Recently, jarosite has been reported on the martian surface based on spectroscopy on the Opportunity rover Christensen et al., 2004 and Klingelhöfer et al., 2004. Although the low temperatures on and near the martian surface are compatible with the preservation of hydrous minerals, the low pressure and low water content of the atmosphere may lead to dehydration. Thus both for the initial formation of jarosite and for its preservation to the present day, one must know the minimum water fugacity under martian pressure–temperature conditions for which jarosite is thermodynamically stable.

The apparent stability of jarosite in terrestrial environment is well known (e.g., Stoffregen, 1993, Dutrizac and Jambor, 2000, Welham et al., 2000 and Arslan and Arslan, 2003) but lack of thermodynamic data till very recently has made it difficult to calculate its stability under martian pressure and temperature conditions. Jarosite on Mars was first postulated by Burns, 1987a, Burns, 1987b and Burns, 1989, Burns and Fisher (1990). Based on literature data (mainly temperature, pH and influence of cation exchange) on the stability of different sulfates, this author considered that Al-bearing jarosite would be sable on the martian surface but the available thermodynamic data were insufficient to prove this assumption.

Based on recently acquired thermochemical data Drouet and Navrotsky, 2003 and Forray et al., 2005, we calculate the equilibrium decomposition curve of jarosite under estimates of present martian pressures and temperatures.

2. Thermodynamic calculations and discussions

The decomposition of jarosite with increasing temperature or decreasing water fugacity occurs by its dehydration (Drouet and Navrotsky, 2003):

$$\underset{\text{(jarosite)}}{KFe_3(SO_4)_2(OH)_6} \rightarrow \underset{\text{(yavapaiite)}}{KFe(SO_4)_2} + \underset{\text{(hematite)}}{Fe_2O_3} + \underset{\text{(water vapour)}}{3H_2O}. \quad (1)$$

High temperature oxide melt solution calorimetry in molten $3Na_2O \cdot 4MoO_3$ at 700 °C has been used successfully to obtain enthalpies of formation of sulphates Navrotsky, 1977, Navrotsky et al., 1994 and Majzlan et al., 2002. Recent data on enthalpies and entropies of formation from the elements and standard entropies of the phases involved in reaction (1) are given in Table 1.

Table 1.

Thermodynamic data used to calculate the stability of jarosite

Compound	ΔH_f° **(kJ mol^{-1})**	S° **(J mol^{-1} K^{-1})**	ΔS_f° **(J mol^{-1} K^{-1})**
$KFe_3(SO_4)_2(OH)_6$ (jarosite)	−3829.6±8.3 [a]	388.9 [b]	−1648.8 [a]
$KFe(SO_4)_2$ (yavapaiite)	−2042.8±6.2 [c]	224.7±5.0 [c]	−751.9±1.0 [c]
α-Fe_2O_3 (hematite)	−826.2±1.3 [d]	87.4±0.2 [d]	
H_2O (gas)	−241.8±0.0 [d]	188.8±0.0 [d]	

[a] (Drouet and Navrotsky, 2003).
[b] (Stoffregen, 1993).
[c] (Forray et al., 2005).
[d] (Robie and Hemingway, 1995).

The yavapaiite heat capacity in the temperature range relevant to Mars is estimated from thermodynamic data on $KAl(SO_4)_2$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, Fe_2O_3, and Al_2O_3 (Forray et al., 2005), using solid state reactions Figs. (2) and (3), under the assumption that the heat capacities of the assemblages on the left and right sides of the reactions are equal (Helgeson et al., 1978).

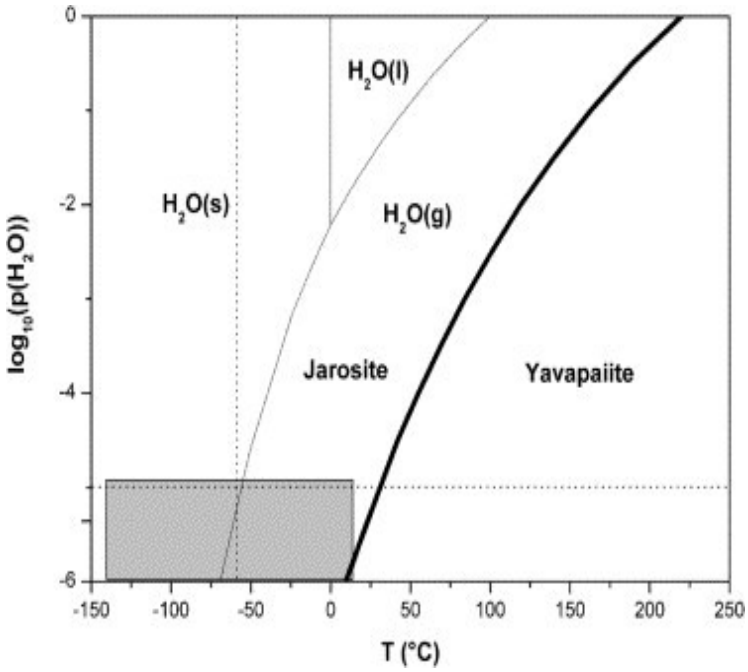
$$2KAl(SO_4)_2 + Fe_2O_3 \rightarrow 2KFe(SO_4)_2 \text{ (yavapaiite)} + Al_2O_3, \quad (2)$$

$$2KAl(SO_4)_2 + Fe_2(SO_4)_3 \rightarrow 2KFe(SO_4)_2 \text{ (yavapaiite)} + Al_2(SO_4)_3. \quad (3)$$

We also calculate, using the same method, the heat capacity of $KAl(SO_4)_2$ and compare it to available experimental data (Barin et al., 1977), in order to estimate the errors involved in this type of heat capacity estimation. For $KAl(SO_4)_2$, this method introduces an error of less than 1% in the heat capacity at temperatures between −150 and 300 °C.

The calculated equilibrium $p(H_2O)$–T curve for reaction (1) is shown in Fig. 1. The total atmospheric pressure estimated and measured Zurek et al., 1992, Burns, 1993, Bridger and Murphy, 1998, Haberle et al., 1999 and Haberle et al., 2003 ranges from 5 to 10 mbar.

Fig. 1. Stability fields of jarosite and yavapaiite under martian pressure and temperature conditions (the partial pressure of water is expressed in atmospheres).



The dotted horizontal line represents the partial pressure of water on the present martian surface, calculated using the abundance of H_2O in the atmosphere Owen et al., 1977, Jakosky and Phillips, 2001 and Bish et al., 2003 and the total atmospheric pressure (Kliore et al., 1965). The dotted vertical line represents the average surface temperature at the equator. The light grey area represents normal surface conditions on Mars at Meridiani Planum, based on measured temperature values (Smith et al., 2004) and calculated values for water vapour pressure. The dark curve represents the phase boundary for reaction (1). The lighter curves represent the H_2O phase diagram. The dark curve barely intersects the light grey area, indicating that jarosite is thermodynamically stable under normal conditions on the present martian surface (Meridiani Planum).

Thermodynamic calculations show that under the low average total atmospheric pressure

(6.76 mbar) on Mars (Haberle et al., 1999), where the partial pressure of H_2O is $\sim 2.5\times10^{-3}$ mbar, the equilibrium decomposition of jarosite to yavapaiite, hematite and water vapour (Eq. (1)) takes place at +18 °C. At the Opportunity landing site at Meridiani Planum, where jarosite was identified (Klingelhöfer et al., 2004), the rover measured temperatures between −91 and +14 °C (Smith et al., 2004) with an uncertainty of measurement less than 0.5 °C. The average surface temperature at the equator is around −58 °C (Kieffer et al., 1977).

Considering that the sedimentary layered formations have low thermal conductivity, it is reasonable to consider any anomalous short-lived temperature above 0 °C to affect only the surface layers. For layered deposits, calculations show that the temperature can quickly decrease by 60 °C in the first 50 cm (Mellon et al., 2004). Thus we conclude that jarosite is within its thermodynamic stability field under present surface conditions on Mars.

Photodecomposition of sulphates by intense solar ultraviolet radiation offers another potential decomposition pathway. Experimental simulation of the photodecomposition of carbonates and sulphates (Mukhin et al., 1996) shows that solar ultraviolet radiation is indeed able to decompose sulphates and may raise the temperature of the minerals by about 25 °C. Such a rise of temperature might bring jarosite to its decomposition boundary, but only in anomalously warm locations. This thermal and/or photocatalysed decomposition will probably be limited to a thin surface layer, and the decomposition products (iron oxide and yavapaiite) on the jarosite surface would probably prevent decomposition below the surface. Thus photodecomposition is probably not a major mechanism for destruction of jarosite on the martian surface.

The initial thermodynamic calculations were done assuming that the jarosite present on Mars is the pure potassium endmember. The quadrupole splittings intensities of Mössbauer spectra recorded by Opportunity rover indicate that the jarosite probably is a K/Na type (Klingelhöfer et al., 2004). This finding is also consistent with the K and Na abundance reported by the rover's alpha particle X-ray spectrometer (Rieder et al., 2004). However, the actual K/Na ratio in the martian jarosite is not known. The thermodynamic effects of this partial sodium substitution or the dehydratation reaction cannot be calculated because, although the energetics of K/Na substitution in jarosite are well know Drouet and Navrotsky, 2003 and Drouet et al., 2004, those in the yavapaiite phase have not been determined. The jarosite mineral inferred from the Opportunity rover explorations is therefore reasonable on both thermodynamic and kinetic grounds. These jarosite minerals persist to the present day because they are thermodynamically stable, but their initial formation presumably required wetter conditions for effective mass transport and crystallisation.

On Earth, there are various pathways for jarosite formation: alteration of Fe bearing sulphates Dutrizac and Jambor, 2000 and Stoffregen et al., 2000, genesis by volcanic activity (alteration of volcanic rocks in acid fumaroles Johnston, 1977, Golden et al., 1996 and Fulignati et al., 2002, or hydrothermal activity (Oue et al., 2002)) with or without bacterial activity Sasaki and Konno, 2000 and Kawano and Tomita, 2001. It is very difficult to present a scenario of jarosite formation on Mars because of lack of information regarding the wider area distribution and types of jarosite occurring on and below the surface. The mineral is found as part of a finely layered sedimentary rock sequence Klingelhöfer et al., 2004 and Squyres et al., 2004 with a concentration of less than 10 wt% within the outcrops (Christensen et al., 2004). The layered sequences themselves appear quite extensive. The presence of igneous rocks on Mars and indications of past volcanic activity (Hartmann and Berman, 2000) indicate that jarosite could have formed in hot-spring or volcanic environments by alteration of basaltic rocks (Burns, 1987a, Burns, 1987b and Burns, 1993. It is not excluded that jarosite could also form in environment similar to impact craters. Regardless of initial formation, post formation transport/redeposition could also have taken place. Jarosite formation requires, in addition to Fe and K (and Na), the presence of water and sulphate at temperatures below 200 °C. Under these conditions, jarosite could achieve stability only if the partial pressure of H_2O were higher (to the left of the dark

curve in Fig. 1) than its present value (horizontal dotted line). It is important to note that jarosite stability does not need liquid water, and jarosite is stable to lower P than the H_2O liquid–vapour or solid–vapour equilibrium. As thermal activity subsided on Mars, the H_2O vapour pressure and surface temperature would have decreased. We suggest that temperature and water vapour pressure decreased in such way that jarosite remained continually in its stability field (the left side of the dark curve in Fig. 1). This constrains a record of environmental changes (variation of temperature and water vapour pressure) on Mars from the time of jarosite formation to the present day. Jarosite age could be determined by measuring the $^{40}Ar/^{39}Ar$ isotopic ratio (Vasconcelos, 1999). This would only be applicable as long as the jarosite contains significant potassium, as would be the case for a mixed (K, Na) phase. Additionally, determination of ^{34}S isotopic composition (Habicht and Canfield, 1996) would provide information about possible biological activity. Arguing that jarosite remained in its thermodynamic stability field at all times, without decomposition or major recrystallisation, we suggest that its morphological (Sasaki and Konno, 2000), chemical, and isotopic Habicht and Canfield, 1996 and Vasconcelos, 1999 signatures may provide clues about the past history of Mars, including evidence of possible biological activity (such as sulphur or iron metabolising microorganisms).

3. Conclusions

Our calculations indicate that jarosite is thermodynamically stable under most present-day martian surface pressures and temperatures. The calculated dehydratation curve gives the relation between maximum temperature and minimum water fugacity through a large part of martian history. Our study highlights the usefulness of this sulphate mineral for understanding the climate, evolution and possible biological activity on Mars. Thus, we suggest the jarosite outcrop on Meridiani Planum should be sampled in any future sample return mission.

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